(12) UK Patent Application (19) GB (11) 2 264 617 (13) A

(43) Date of A publication 01.09.1993

(21) Application No 9220324.9

(22) Date of filing 25.09.1992

(30) Priority data
(31) 9121312 (32) 08.10.1991 (33) GB

(51) INT CL5
H05B 3/12, C23C 14/06 16/06 16/22 // C23C 16/32 16/42

(52) UK CL (Edition L)
H5H HCB H100 H103 H109 H121 H122 H123 H124 H126 H144 H251
C7F FHB FP902 FR861 FR902 FR905 FR916 F809
U1S S1953 S1976

(56) Documents cited
GB 2111809 A GB 1386551 A

(58) Field of search
UK CL (Edition K) C7F FBAX FBBX FBXX FCSX FCXX FHE FHZ FPCX FPDX FPEX, H5H HAX2 HCA HCB
INT CL5 C23C 14/06 16/22 16/32 16/42, H05B 3/10 3/12 3/14
Online databases: WPI, CLAIMS

(71) Applicant
United Kingdom Atomic Energy Authority

(Incorporated in the United Kingdom)

Patents Department, Building 329, Harwell Laboratory, Didcot, Oxfordshire, OX11 0RA, United Kingdom

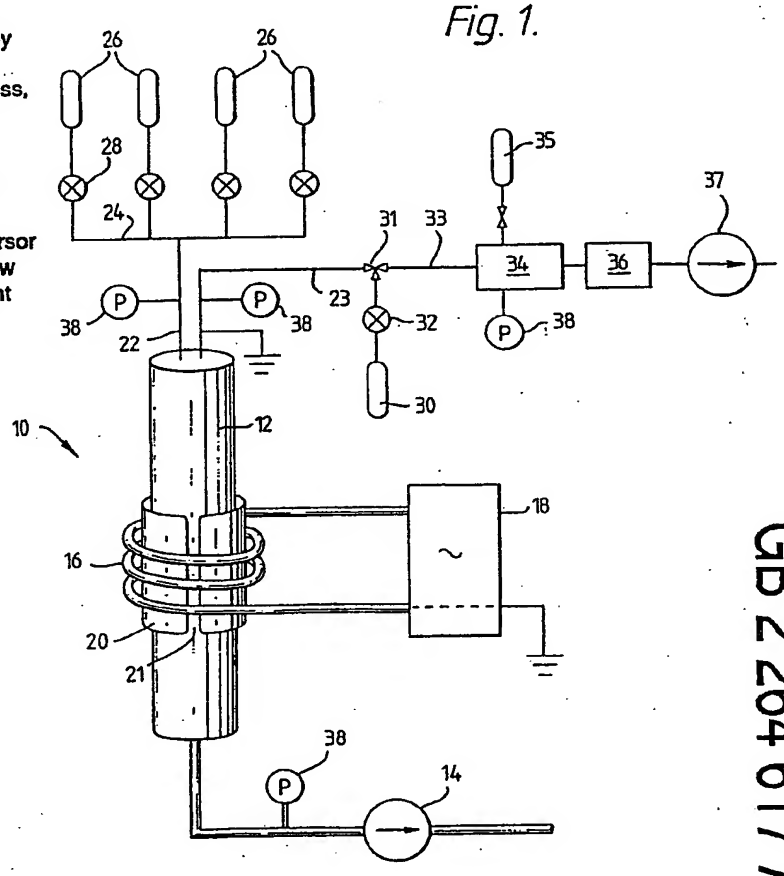
(72) Inventor
David Stafford Rickerby

(74) Agent and/or Address for Service
Peter Turquand Mansfield
United Kingdom Atomic Energy Authority,
Patents Department, Building 329, Harwell Laboratory, Didcot, Oxfordshire, OX11 0RA, United Kingdom

(54) Porous heating element

(57) A porous electric heating element is made by coating a fibrous carbon precursor with carbon, silicon and titanium by a vapour deposition process, preferably a plasma activated vapour deposition process. The coating comprises silicon carbide, titanium carbide and titanium silicide, and its temperature coefficient of resistance can be less negative than that of known silicon carbide elements, or even be positive. The carbon precursor may then be removed by oxidation to leave hollow tubular fibres of the coating material. The element may be used to heat a fluid electrically.

Fig. 1.



GB 2 264 617 A

Fig. 1.

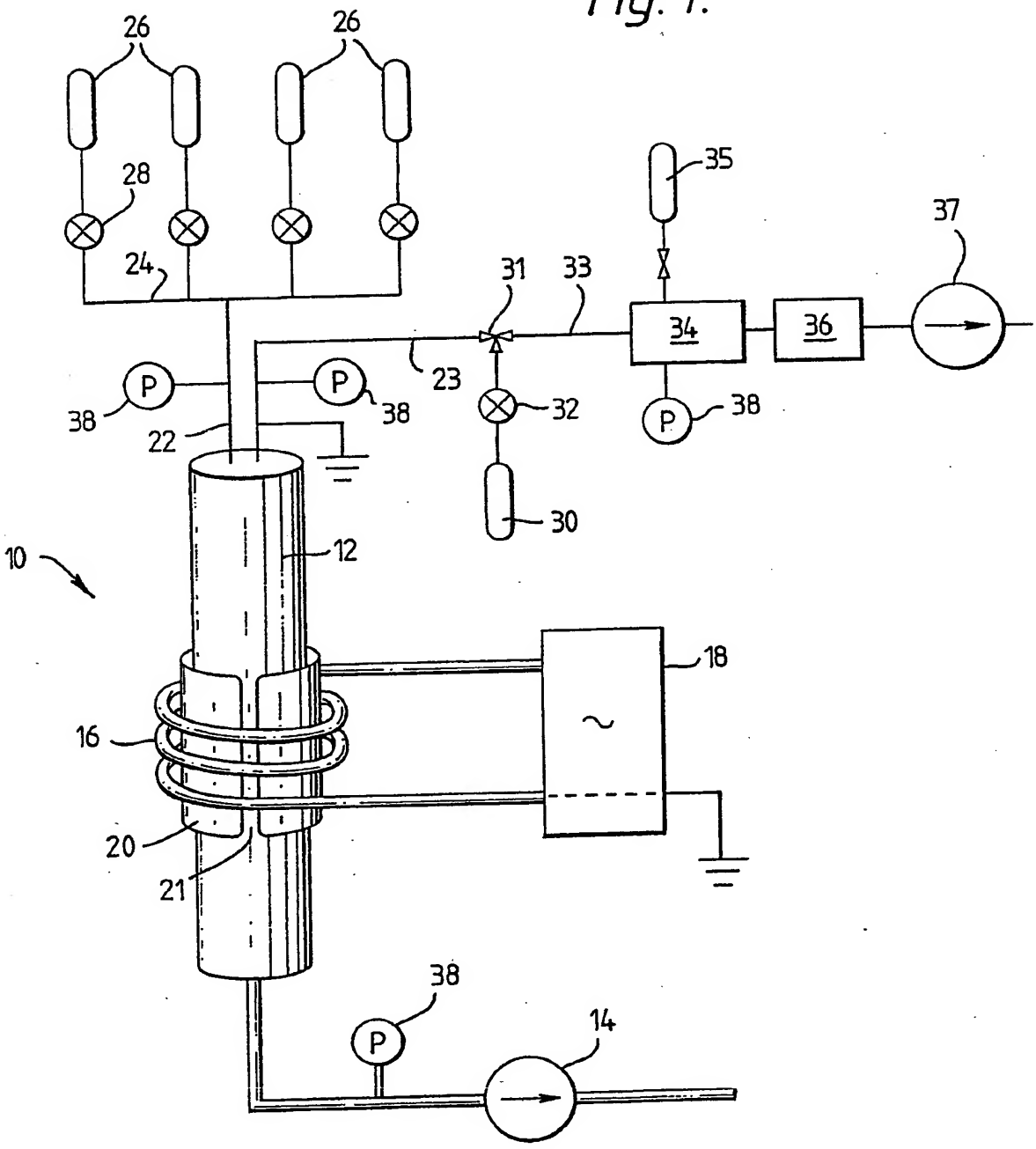
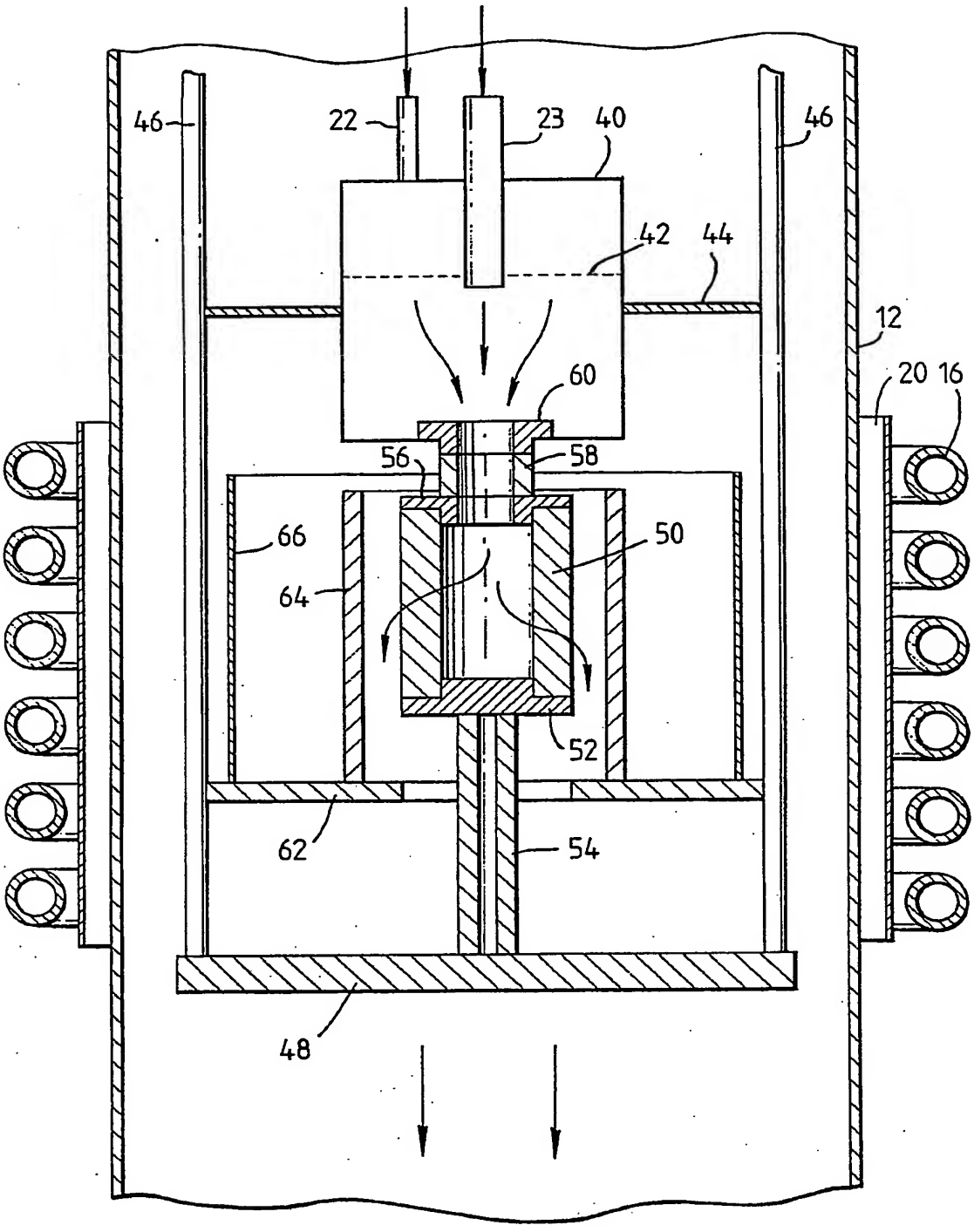

26
26
28
24
35
37
31
33
34
36
23
38
38
22
32
38
30
10
12
18
16
20
21
38
14

Fig. 2.



Porous Heating Element

This invention relates to a fluid-permeable fibrous electric heating element, and to a process for making such elements.

Fluid heating systems in which heat is generated by an electric current flowing through a fluid-permeable electrically conductive element, and is transferred to a fluid permeating and flowing through the element, are known. Where the element is a fibrous material with the voids between the fibres providing the fluid path the element can provide high power densities in excess of 1 kW/cm^3, combined with little resistance to the fluid flow as a result of high voidages of between 50 and 98 percent, for example. Such an element has low thermal capacity, so that it can provide a rapid response time where a change of heater power is desired.

UK patent GB 1 600 253 describes a method of making one such element, in which a body is formed of randomly disposed carbonisable fibres (for example of polyacrylonitrile) to which a latent solvent is applied, the solvent is then activated to bond the fibres together, and the fibres are then carbonised. The element so produced consists of a rigid structure of carbon fibres. As described in GB 2 111 809 this fibrous carbon element may be used as a precursor in the manufacture of other types of elements, the carbon fibres being coated by a plasma assisted vapour deposition process with a material comprising silicon or silicon and carbon (primarily as silicon carbide). The original fibrous carbon precursor may either be retained, or removed by oxidation so that a structure of tubular fibres of the deposited material remains. A suitable heat treatment may be used to adjust the electrical conductivity and the temperature coefficient

of resistance of the deposited material to desired values. The fibrous carbon elements and the fibrous silicon or silicon carbide elements, made by the processes described in these two patents, can provide the advantages of high power density, low fluid pressure drop, and rapid response, as outlined above, but have a negative temperature coefficient of resistance. Consequently their resistance decreases as their temperature rises, so that controlling the electrical current through them in operation is more complex than with conventional metallic heating elements.

According to the present invention there is provided a process for making a fluid-permeable fibrous electric heating element, the process comprising depositing from the gas phase onto a fibrous carbon precursor a coating comprising silicon, titanium and carbon.

Preferably the deposition is performed by plasma-assisted chemical vapour deposition (PACVD), as this enables the deposition to be performed at lower temperatures than are necessary for chemical vapour deposition (CVD), for example between 700 and 900°C for PACVD compared to over 900°C for CVD. This is because the plasma assists the breakdown of the reactant gases to form radicals or ions. Desirably deposition is continued until the coating is between 0.1 and 30 micrometres thick, preferably between 1 and 5 micrometres thick. The coating may also comprise a dopant material to modify its electrical resistivity. The electrical properties of the element can be controlled by adjusting the proportions of silicon, titanium and carbon which are deposited, and by heat treatment. The elemental proportions determine the proportions of the various deposited phases, which are primarily silicon carbide, titanium carbide, and one or more titanium silicides, while the heat treatment affects the grain structure of the coating. The carbon fibre

precursor can be removed by an oxidation process to leave tubular fibres of the coating material.

The deposition process may rely on diffusion to ensure the reactant gases permeate the precursor and deposit the coating throughout the thickness of the precursor. Alternatively the reactant gases may be caused to flow through the precursor by a pressure difference between opposite surfaces; where the precursor is of annular or tubular form, the gases may be supplied to the bore of the precursor and caused to flow radially outward to the outer surface of the precursor (or vice versa). The process is substantially the same as those referred to as plasma-assisted or isothermal chemical vapour infiltration, although in the process of the invention the deposition is preferably terminated while the voidage is high. As deposition proceeds the pressure difference increases, and the process may be monitored by monitoring the pressure difference. The degree of uniformity of the coating thickness through the element may be controlled by controlling the temperature of the precursor, the gas flow rate, and the pressure at the inlet suface of the precursor; a more uniform coating is generally obtained if the chemical reactions occur at a slower rate, and this can be achieved by reducing the temperature (so the sticking coefficient increases), by increasing the gas flow rate (so the residence time decreases), or by increasing the internal pressure (to increase the recombination rate in the gas phase).

The present invention also provides a fluid-permeable fibrous electric heating element comprising a structure constituted by fibres of a material comprising silicon, titanium and carbon, the fibres either having a carbon core or being hollow tubes.

The element of the invention which may be made by the above-defined process, depending on the proportions of the deposited phases and on the grain structure, may have a temperature coefficient of resistance either less negative than that of the silicon carbide elements of the prior art, or even positive. Consequently it is much easier to use, especially in high-power or high-temperature applications, as it is relatively easy to control the electric current through it. Hence the power supply needed, where such an element is used to heat a fluid, can be simpler and cheaper than with previously known fibrous heating elements.

The invention will now be further described, by way of example only, and with reference to the accompanying drawings in which:

Figure 1 shows a diagrammatic perspective view of an apparatus for making a fluid-permeable fibrous electric heating element; and

Figure 2 shows a longitudinal sectional view of part of the apparatus of Figure 1.

Referring to Figure 1 an apparatus 10 includes an upright silica tube 12 sealed at each end, which can be evacuated by a vacuum pump 14. Around a central portion of the tube 12 is a multi-turn coil 16 of water-cooled copper tube whose ends are connected to terminals of a high voltage high frequency signal generator 18 (8kV, 345 kHz, up to 45 kW). Between the coil 16 and the tube 12 is a water-cooled, thin copper electrode 20 of cylindrical form, but with a longitudinal slot 21 to minimize eddy current heating. Two stainless steel gas lines 22, 23 enable gases to be supplied to one end of the tube 12. One gas line 22 connects to a mixing manifold 24 to which are connected supplies 26 of argon, hydrogen, silane, and ethene gas via

respective metering valves 28. The other gas line 23 is trace-heated along its length to 80°C, and is connected to a heated boiler 30 via a switch-over valve 31 and a vapour source controller 32; the boiler 30 generates titanium tetrachloride vapour. The switch-over valve 31 enables the vapour to be supplied either to the gas line 23, or to a bypass line 33 which connects to a chamber 34 supplied with a bleed of argon gas from a source 35, hence to a cold trap 36 for condensing the titanium chloride, and hence to a vacuum pump 37. Pressure gauges 38 enable the pressures at the gas lines 22 and 23, the chamber 34, and at the duct connected to the vacuum pump 14 to be monitored. One end of the coil 16 is earthy (i.e. earthed within the generator 18, at least as regards ac), and the gas lines 22 and 23 are earthed.

Referring now to Figure 2 there is shown to a larger scale a sectional view of the central portion of the tube 12. The gas lines 22 and 23 both communicate with a stainless steel mixing chamber 40; the line 23 communicates directly with the lower half of the chamber 40 whereas the line 22 communicates through a perforated stainless steel plate 42. The chamber 40 has an external flange 44 by which it is clamped to two graphite coated alumina support rods 46 fixed at their top ends to the means sealing the upper end of the silica tube 12. The bottom ends of the rods 46 are connected by a stainless steel bar 48. An annular or tubular carbon fibre precursor 50 (which may be made as described in GB 1 600 253, as outlined above) is clamped between the bar 48 and the bottom of the mixing chamber 40: the lower end of the precursor 50 is blocked by a graphite end plate 52 supported on a graphite-coated alumina tube 54, while the upper end of the precursor 50 mates with an annular graphite ring 56 spaced apart, by a graphite-coated alumina tube 58, from a similar graphite ring 60 locating in an aperture in the bottom of the mixing

chamber 40 to which it forms a gas-tight seal.

An annular graphite plate 62 is supported by the rods 46 above the bar 48, to provide a support for two cylindrically tubular components which surround the precursor 50. These components are a graphite tube or susceptor 64, outside which is a thin stainless steel heat shield 66; the shield 66 has a longitudinal slot to minimize eddy current heating. By virtue of the earth connection to the gas line 23, and the graphite coating on the alumina rods 46 and tubes 54 and 58, all the components within the tube 12 are earthed.

In operation, the apparatus 10 is assembled as shown in the Figures, and by means of the pumps 14 and 37 the tube 12 and the chamber 34 are evacuated. Argon is bled into the chamber 34 and the pump 37 arranged to hold the pressure at 7.5 torr (1 kPa). The titanium chloride boiler 30 is energised, and the valve 31 arranged so the vapour is supplied to the by-pass line 33 and so to the chamber 34 (this gives time for operation of the boiler 30 to stabilize). Argon and hydrogen are supplied to the gas line 22 and the pump 14 arranged to hold the pressure in the tube 12 at 3.5 torr (0.47 kPa). The signal generator 18 is energised, with the electrode 20 connected electrically to the mid-point of the coil 16. The graphite susceptor 64 is heated inductively to for example 750°C (this temperature might be between say 700° and 1000°C), and plasma is generated in the vicinity of the precursor 50 which leads to reduction of surface oxides, and can improve adhesion of the coating. The precursor 50 is heated by radiation from the susceptor 64 to substantially the same temperature as the susceptor 64.

Silane and ethene are then supplied to the gas line 22, and the pump 14 arranged to hold the pressure in the

gas line 22 to 7.5 torr (1kPa), and the valve 31 is switched over so the titanium tetrachloride vapour is supplied to the gas line 23, so as to mix with the other gases in the mixing chamber 40. The molecules in the gases are broken down (into radicals or ions) as a result of both the high temperature and the plasma. Carbon, silicon and titanium atoms are consequently deposited onto the fibres which constitute the precursor 50. The resultant coating is believed to consist principally of silicon carbide, titanium carbide, and titanium silicide, although the exact formulae of the phases are not known. The thickness of the coating depends on how long the coating process is continued, as a coating deposition rate of around 0.1 micrometres/minute can be achieved. The process can be monitored by monitoring the pressure difference between the inside and the outside of the precursor 50. By way of example the gas flow rates, measured in standard cubic centimetres per minute, might be as follows: argon 1000, hydrogen 300, silane 10, ethene 10, and titanium tetrachloride vapour 15.

The energy provided to the plasma can be adjusted by moving the electrical connection between the coil 16 and the electrode 20. However, if the electrode 20 is connected to a good earth, then although the susceptor 64 will still be heated inductively no plasma will be formed, and only CVD will occur. It has been found that the PACVD process produces more deposition of titanium than CVD, so the method of the invention preferably utilizes a plasma.

After the coating process has been completed the coated precursor 50 is removed from the apparatus 10. Usually the carbon fibres are then burnt out by heating in air to 770°C, in a furnace whose temperature is raised at 1.5°C/min, and then held at tht temperature for 16 hours. After cooling, the resulting ceramic fibrous element may

then be heat treated, for example it may be annealled in argon at 1300°C for 48 hours to reduce its resistance to a desired value.

It will be appreciated that the gases supplied to the apparatus 10 to bring about deposition of silicon, titanium and carbon as specified above are by way of example only, and that alternative gases may be used. For example $Ti(OCH_3)_3$ might be used as an alternative to $TiCl_4$.

Claims

1. A process for making a fluid-permeable fibrous electric heating element, the process comprising depositing from the gas phase onto a fibrous carbon precursor a coating comprising silicon, titanium and carbon.

2. A process as claimed in Claim 1 wherein the deposition is performed by plasma-assisted chemical vapour deposition.

3. A process as claimed in Claim 1 or Claim 2 wherein the deposition is continued until the coating is between 0.1 and 30 micrometres thick, preferably between 1 and 5 micrometres thick.

4. A process as claimed in any one of the preceding Claims also comprising a subsequent step of removing the precursor by oxidation to leave tubular fibres of the coating material.

5. A fluid-permeable fibrous electric heating element comprising a structure constituted by fibres of a material comprising silicon, titanium and carbon, the fibres either having a carbon core or being hollow tubes.

6. A process for making a fluid-permeable fibrous electric heating element substantially as hereinbefore described with reference to, and as shown in, the accompanying drawings.

7. A fluid-permeable fibrous electric heating element made by a process as claimed in any one of Claims 1 to 4 or Claim 6.

Patents Act 1977
Examiner's report to the Comptroller under ction 17 (The Search Report)

Application number

GB 9220324.9

Relevant Technical fields

(i) UK Cl (Edition K) H5H, HAX2, HCA, HCB, C7F, FBAX FBBX, FBXX, FCSX, FCXX, FHE, FHZ, FPCX, FPDX, FPEX

(ii) Int Cl (Edition 5) H05B 3/10, 3/12, 3/14, C23C 14/06, 16/22, 16/32, 16/42

Search Examiner

R W BALDOCK

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CLAIMS

Date of Search

23 NOVEMBER 1992

Documents considered relevant following a search in respect of claims 1-7

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	GB 2111809 A (UKAEA) See especially page 4 line 3 - page 5 line 5	1-5, 7
Y	GB 1386551 (UNITED AIRCRAFT) See especially Example 6	1-3, 5, 7

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

Published 1993 at The Patent Office, Concept House, Cardiff Road, Newport, Gwent NP9 1RH. Further